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16. ABSTRACT

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The data indicates a mean percent bias of 30% or less was achieved for most of the audit compounds sampled by Tenax. The results also show that the canister sampler cannot be adequately evaluated using volatile organics in dry nitrogen because of absorption losses of certain compounds. Several of the less volatile compounds in the audit gas exhibited significantly reduced recovery or were not detected after being sampled by the canister. Recovery of highly volatile compounds in the gas was quantitative. Further investigation showed that the use of humidified audit gas resulted in the quantitative recovery of all the VOC's that were sampled by the canister.

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Abstract

Performance audit results of two different ambient air monitoring projects for volatile organic compounds (VOC's) are presented. An NBS traceable gas cylinder containing several VOC's in dry nitrogen at parts per billion (ppb) concentration levels was used at the field sampling site to evaluate performance of the sampling and analytical systems. Both Tenax cartridges and evacuated stainless steel canisters (6 litre) were used to sample the air. Sample media exposed to the audit gas were returned to the laboratory for analysis.

The data indicates a mean percent bias of 30% or less was achieved for most of the audit compounds sampled by Tenax. The results also show that the canister sampler cannot be adequately evaluated using volatile organics in dry nitrogen because of absorption losses of certain compounds. Several of the less volatile compounds in the audit gas exhibited significantly reduced recovery or were not detected after being sampled by the canister. Recovery of highly volatile compounds in the gas was quantitative. Further investigation showed that the use of humidified audit gas resulted in the quantitative recovery of all the VOC's that were sampled by the canister.

Introduction

The Quality Assurance Division of the Environmental Monitoring Systems Laboratory (EMSL), U.S. EPA has the responsibility for conducting performance audits of the various ambient air monitoring studies undertaken by the laboratory. In these studies evacuated canisters and Tenax cartridges are frequently used to sample for volatile organic compounds (VOC's) in the ambient air. Cylinder gases filled with selected VOC's that are traceable to the National Bureau of Standards (NBS) are used to assess the performance of the sampling and analytical systems of these projects. The audit cylinders and/or canisters are transported to the field sampling site and used to challenge the sampling system with known concentrations of VOC's in the audit gas. It was discovered that certain less volatile compounds in the audit gas were not recovered from a canister sampler when dry gas was used for the audit. However, when the gas was humidified by adding a small amount of water to the audit canister, quantitative results were obtained. Previous articles have reported on efforts to audit Tenax samplers with NBS-traceable gas cylinders containing VOC's [1,2]. The use of evacuated stainless steel canisters to sample for pollutants in the ambient air offers certain advantages over Tenax cartridges such as replicate analyses, no breakthrough of compounds and avoidance of artifact formation. This article describes the results of field audits of two different air monitoring projects in which the performance of canister and Tenax samplers was evaluated using gas mixtures containing low parts-per-billion (ppb) concentrations of VOC's.

Experimental

The identity and concentrations of compounds in the NBS prepared gas cylinder (in dry nitrogen) are listed in Table 1. The total uncertainties

next to the concentrations represent the estimated 95% confidence limits in ppb. The audit gas was used undiluted. For a recovery study on a canister sampler, a canister containing the audit gas was humidified by manually adding with a syringe 8 mg water per litre of gas volume in the canister. The canister was pressurized to 30 psig (18 litre) so the amount of water added was 144 mg. The canister sampler inlet was connected to an audit canister or gas cylinder with 3 mm O.D. 316 SS tubing and sampled at 90 mℓ/min. for 2 hours. The Tenax sampler was connected to the audit gas via a transfer line that supplied gas to the four separate Tenax tubes each operated at a different flow rate as described previously [2]. Gas was sampled through the sampler at flow rates from 10 mℓ/min. for 2 hours. The canister samples were analyzed using cryogenic preconcentration and a gas chromatograph equipped with flame ionization/electron capture detectors [3]. The Tenax samples were analyzed using thermal desorption and combined gas chromatography/mass spectrometry [4].

Results and Discussion

Canister Sampler Audit

The analyses results on the audit of a canister sampler appears in Tables 2 and 3. Two consecutive runs using undiluted dry gas were made on the sampler and the canisters were analyzed by Northrop Services, Inc. (NSI) and Battelle-Columbus Laboratories. Table 3 contains only the study target compounds that were in the audit gas, but NSI analyzed several more compounds in the gas. The VOC's are listed in order of decreasing volatility. The percent biases are low for the more volatile compounds but the less volatile VOC's exhibited significantly higher biases indicating large losses. The

lower biases in Run 2 probably were due to a "conditioning" of the sampler during the first run causing it to adsorb less material from the run immediately following it.

Before the reasons for the low recoveries of certain VOC's could be investigated, it was necessary to perform field audits on two canister samples. This time, as part of the audit, one of the canisters was filled directly while the others were filled by passing the gas through the sampler. The canister filled directly served as a control, that is, as a comparison of its analytical recoveries for VOC's to that for canisters where gas had passed through the sampler. The results, in Tables 4 and 5, clearly indicate that the losses of certain VOC's occurred when the gas was passed through the samplers and not in the canister itself. As occurred in the previous audit, the largest losses were observed with the less volatile VOC's in the audit mixture. Certain compound losses were so large that they were totally adsorbed in the sampler.

In order to determine the effect of moisture on the recovery of VOC's through the sampler, a canister was prepared containing the audit gas and 8 mg/ℓ of water. This gas mixture was sampled by a canister sampler and analyzed as in the previous audits. The results in Table 6 show excellent recovery for all VOC's in the gas and indicate that humidified gas could be used to achieve valid audit data on certain less volatile compounds when conducting field evaluations on canister samplers.

Tenax Sampler Audit

The results of the Tenax sampler audit are listed in Table 7. From 100 ng to 1500 ng was delivered to the sampler with each tube receiving a different amount of audit gas based on the flow rate. The percent bias results from each of the four sample tubes were averaged to obtain the mean

percent bias and were also used to calculate the standard deviation. These results indicate that both sampling and analyses of VOC's using Tenax tubes was performing properly and within expectations.

Conclusions

Audit gas mixtures of VOC's have been successfully used to evaluate the performance of canister and Tenax ambient air samplers. By introducing the audit gas into the sampler at the field sampling location, the complete system of sampling and analytical operations can be evaluated. The audits of canister samplers with an NBS prepared gas cylinder at field sampling sites revealed that certain less volatile compounds in the dry gas mixture were not recovered through the systems. It was determined that adding water to the gas to humidify it resulted in quantitative recoveries of all the VOC's in the audit gas. The results from an audit on a Tenax sampler indicated that the sampling and analysis operations were within expectations.

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Table 1. Audit Gas Compounds and Concentrations

Compound	Concentration, ppb (by mole)
vinyl chloride	7.5 ± 1.1
bromomethane	17.7 ± 0.9
trichlorofluoromethane	12.7 ± 0.7
chloroform	15.5 ± 0.6
1,1,1-trichloroethane	11.0 ± 0.3
carbon tetrachloride	12.6 ± 0.8
benzene - d_6	16.6 ± 1.0
1,2-dichloroethane	10.2 ± 1.4
trichloroethylene	15.2 ± 0.7
1,2-dichloropropane	9.4 ± 0.7
toluene - d_8	11.0 ± 0.5
tetrachloroethylene	12.6 ± 1.2
1,2-dibromoethane	5.0 ± 0.4
chlorobenzene	11.8 ± 0.4
ethylbenzene	9.1 ± 0.7
o-xylene	11.7 ± 0.7
styrene	10.2 ± 2.8

Table 2. Kanawha Valley Study

Analyses of Canister Dry Gas Audit Samples
(Northrop)

Compound	Concentration, ppb			Bias, %	
	Audit Gas	Run 1	Run 2	Run 1	Run 2
vinyl chloride	7.4	7.6	8.0	2.7	8.1
bromomethane	17.4	17.3	18.2	-0.6	4.6
trichlorofluoromethane	12.4	13.1	12.8	5.6	3.2
chloroform	15.7	14.2	14.2	-9.6	-9.6
1,1,1-trichloroethane	10.7	9.1	8.9	-15	-17
carbon tetrachloride	12.4	11.6	11.5	-6.5	-7.3
1,2-dichloroethane	10.3	9.4	9.8	-8.7	-4.9
trichloroethylene	15.2	13.7	13.9	-9.9	-8.6
1,2-dichloropropane	9.2	6.3	8.1	-32	-12
tetrachloroethylene	12.9	10.4	11.0	-19	-15
1,2-dibromoethane	5.0	1.4	2.6	-72	-48
chlorobenzene	11.8	5.4	8.3	-54	-30
ethylbenzene	8.8	0.8	4.3	-91	-51
o-xylene	12.0	0.4	4.6	-97	-62

Table 3. Kanawha Valley Study

Analyses of Canister Dry Gas Audit Samples
(Battelle)

Compound	Concentration, ppb			Bias, %	
	Audit Gas	Run 1	Run 2	Run 1	Run 2
vinyl chloride	7.4	4.9	5.1	-34	-31
chloroform	15.7	15.3	15.7	-2.5	0.0
1,1,1-trichloroethane	10.7	11.0	11.3	2.8	5.6
carbon tetrachloride	12.4	12.4	12.6	0.0	1.6
1,2-dichloroethane	10.3	8.4	9.3	-18	-9.7
trichloroethylene	15.2	16.2	16.8	6.6	10
tetrachloroethylene	12.9	13.0	13.9	0.8	7.8
1,2-dibromoethane	5.0	1.7	3.3	-66	-34
chlorobenzene	11.8	7.5	12.1	-36	2.5
o-xylene	12.0	0.3	4.6	-97	-62

Table 4. Toxic Air Monitoring Study

Analyses of Canister Dry Gas Audit Samples
(Northrop)

Compound	Concentration, ppb			
	Audit Gas	Canister Only	Sampler No. 1	Sampler No. 5
vinyl chloride	7.4	6.5	7.8	8.2
bromomethane	17.4	18.0	17.4	16.8
trichlorofluoromethane	12.4	11.3	12.2	12.2
chloroform	15.7	14.3	15.2	14.0
1,1,1-trichloroethane	10.7	10.0	10.6	9.3
carbon tetrachloride	12.4	12.2	13.1	12.1
benzene - d_6	16.6	15.9	18.4	12.3
1,2-dichloroethane	10.3	10.7	10.6	5.5
trichloroethylene	15.2	14.3	15.3	12.7
1,2-dichloropropane	9.2	8.3	1.4	1.8
toluene - d_8	11.0	9.4	0.8	0.9
tetrachloroethylene	12.9	12.4	14.0	9.1
1,2-dibromoethane	5.0	4.3	ND	ND
chlorobenzene	11.8	11.1	0.3	0.5
ethylbenzene	8.8	8.8	ND	ND
o-xylene	12.0	9.6	ND	ND
styrene	11.8	14.8	ND	ND

ND - not detected

Table 5. Toxic Air Monitoring Study

Analyses of Canister Dry Gas Audit Samples
(Northrop)

Compound	Bias, % Canister Only	Sampler No. 1	Sampler No. 5
vinyl chloride	-12	5.4	11
bromomethane	3.4	0.0	-3.4
trichlorofluoromethane	-8.9	-1.6	-1.6
chloroform	-8.9	-3.2	-11
1,1,1-trichloroethane	-6.5	-0.9	-13
carbon tetrachloride	-1.6	5.6	-2.4
benzene - d_6	-4.2	11	-26
1,2-dichloroethane	3.9	2.9	-47
trichloroethylene	-5.9	0.7	-16
1,2-dichloropropane	-9.8	-85	-80
toluene - d_8	-15	-93	-92
tetrachloroethylene	-3.9	8.5	-29
1,2-dibromoethane	-14	--	--
chlorobenzene	-5.9	-97	-96
ethylbenzene	0.0	--	--
o-xylene	-20	--	--
styrene	25	--	--

Table 6. Recovery of Volatile Organic Compounds Through a Canister Sampler Using Humidified Audit Gas

Compound	Concentration, ppb		
	Audit Gas Humidified	Run 1	Bias, %
vinyl chloride	6.2	6.0	-3.2
bromomethane	17.8	19.9	12
trichlorofluoromethane	13.6	14.0	2.9
chloroform	14.1	13.8	-2.1
1,1,1-trichloroethane	9.3	9.1	-2.1
carbon tetrachloride	12.6	12.5	-0.8
benzene - d_6	15.0	14.6	-2.7
1,2-dichloroethane	10.2	10.2	0.0
trichloroethylene	12.7	12.4	-2.4
1,2-dichloropropane	8.2	8.2	0.0
toluene - d_8	8.9	8.7	-2.2
tetrachloroethylene	11.0	10.8	-1.8
1,2-dibromoethane	4.5	4.6	2.2
chlorobenzene	9.4	9.3	-1.1
ethylbenzene	8.0	7.8	-2.5
o-xylene	9.1	9.0	-1.1
styrene	13.6	13.6	0.0

Table 7. Kanawha Valley Study

Results of Tenax Sampler Audit

Compound	EMSL (1 run) Mean Bias, %	EMSL (1 run) Std. Dev.	Battelle (2 runs) Mean Bias, %	Battelle (2 runs) Std. Dev.
chloroform	-26.5	13.5	-10.1	11.6
1,1,1-trichloroethane	-19.6	22.0	8.8	11.7
carbon tetrachloride	-48.2	11.8	-8.1	9.2
1,2-dichloroethane	-34.1	11.2	-12.4	8.8
trichloroethylene	-0.6	19.8	-1.2	7.7
tetrachloroethylene	10.3	1.5	-9.2	8.6
1,2-dibromoethane	17.3	59.8	6.6	4.2
chlorobenzene	-2.0	3.6	5.2	5.9
o-xylene	-13.9	4	3.6	5.1
benzene - d_6	-17.2	18.0	---	---
toluene - d_8	0.2	5.7	---	---
1,2-dichloropropane	16.6	27.8	---	---
ethylbenzene	-13.2	3.3	---	---
styrene	-18.0	2.9	---	---